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(54) Title: DYNAMERS: POLYMERIC MATERIALS EXHIBITING REVERSIBLE FORMATION AND COMPONENT EXCHANGE

(57) Abstract: Alternating co-polymers involving the polycondensation of dihydrazides or diamines with dialdehydes reversibly exchange either one or both of their fundamental repeating monomer units in the presence of different monomer units. Furthermore, upon exchange of one of the repeating monomer units, the original monomer unit displaced can be re-introduced into the polymer, or the remaining unexchanged original monomer unit may also be interchanged. The polymers subjected to monomer exchange/interchange exhibit vastly different physical properties than those of the original unexchanged polymer. These dynamic, reversible polymers are therefore able to incorporate, decorporate or reshuffle their constituting monomers, in particular, with respect to environmental physical or chemical factors (heat, light, chemical entities, etc.). They thus have combinatorial features and represent adaptive materials.

DYNAMERS: POLYMERIC MATERIALS EXHIBITING REVERSIBLE FORMATION AND COMPONENT EXCHANGE

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1-11

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Abstract

Alternating co-polymers involving the polycondensation of dihydrazides or diamines with dialdehydes reversibly exchange either one or both of their fundamental repeating monomer units in the presence of different monomer units. Furthermore, upon exchange of one of the repeating monomer units, the original monomer unit displaced can be re-introduced into the polymer, or the remaining unexchanged original monomer unit may also be interchanged. The polymers subjected to monomer exchange/interchange exhibit vastly different physical properties than those of the original unexchanged polymer. These dynamic, reversible polymers are therefore able to incorporate, decorporate or reshuffle their constituting monomers, in particular, with respect to environmental physical or chemical factors (heat, light, chemical entities, etc.). They thus have combinatorial features and represent adaptive materials.

Field of The Invention

The invention described herein relates to polymers generated through the formation of reversible covalent connections between the monomeric constituents. In particular, it implements carbon-nitrogen double bond formation occurring between amine (amines, hydrazines, hydrazides, oximes, etc.) and carbonyl (aldehydes, ketones, etc.) functional groups. It can be represented by the following scheme where R_1, R_2, R_3 are hydrocarbon or heteroatomic groups and X may be N, O, N-(C=O)-, S, or C sites.

Scheme 1

The present invention concerns, but is not limited to, polymers of the type being poly(acyl and/or aryl)hydrazides (currently known as polyhydrazones) and polyimines. The said polymers are composed of co-alternating repeating units via the polycondensation of dialdehydes with diamines and/or dihydrazides, here forth known as *Dynamers*, related to the invention in their capability of sustaining reversible exchange of one or both of the their fundamental repeating units in the presence of different free monomer units. The exchange process is here forth defined as *Dynamerization*. The polymer exchange, i.e. *Dynamerization*, can involve one or both of the polymer fundamental repeating units, which can be done with heat and with or without catalysis (acid or other). This invention also concerns the process of Dynamers capable of exchanging their monomer units in the presence of a second Dynamer leading to two new Dynamers different than the originals by cross-polymerization, i.e. cross-Dynamerization. The terms interchange and exchange are used synonymously throughout. In principle, any chemical reaction involving reversible covalent bond formation (as in disulfides, aldols, olefin metathesis, boronic esters; etc.) may be implemented in the generation of Dynamers.

Applications of Invention

The invention of this patent can be applied in the following applications: thermal sensors, wear-and-tear/degradation sensors, heat sensors, decomposition sensors, adhesives, adhesive sensors, self-repairable and/or auto-amendable polymers, interchangeable polymeric components for automotive or cellular phone industry, photoluminescence devices, electroluminescence devices, organic light emitting diodes, conductive materials, conducting polymers, plastic wires, organic wires, high-through put polymer screening for generating libraries of conducting polymers or organic light emitting diodes, biomedical conducting electronic devices for *in-vivo* purposes, drug delivery vesicles, artificial DNA, amplification of genetic codes, disease identification tests.

Background of The Invention

Reversible, also known as dynamic, reactions are widespread in chemistry and biology, ranging from intra/ntermolecular hydrogen bonds to covalent ones. The latter is readily exploited for protecting functional groups in organic synthesis allowing modification of the molecule without altering the group protected. Under mild conditions, the protected group can be removed whereby regenerating the original pre-protected functionality. Of the many known covalent reversible reactions (see Rowan et al. for review dynamic chemistry), the hydrazone reaction involving the addition of a hydrazide and an aldehyde is reversible, shown in Scheme 2, is acid catalyzed, but the presence of excess water under acid conditions regenerates the starting materials.

Scheme 2

The reversibility of the hydrazone reaction can be extended where in the presence of an additional aldehyde or hydrazide, a new hydrazone can result from aldehyde exchange as depicted in Scheme 3. Typical conditions promoting exchange involve acid catalysis and/or heat. This approach has previously been applied in the field of polymers as described in US patent 4 210 565 and UK patent 2 295 781 where the radicals R_1 and R_3 where polymeric in nature. The applicants of the cited patents described the reaction leading to a polyhydrazone (*sic* Scheme 2) and the exchange/interchange of an aldehyde leading to a new polyhydrazone for the purposes of creating a cross-linked network (curing) for increased viscosity and increased molecular weight. It should be noted that the cited polyhydrazone reactions involved pendant groups from the polymer backbone (i.e. orthogonal groups), where no interchange involving the fundamental repeating units of the polymer backbone occurred.

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Scheme 3

The reaction involving imines (see Scheme 4) is yet another reaction that is reversible, but is more sensitive to pH than its hydrazone analogue. The equilibrium can greatly be influence by the pH, where the equilibrium lies to the side of the reagents at low pH and the to the products in alkaline medium. Similarly to the hydrazones, an exchange involving the incorporation of an aldehyde or amine leading to a new imine is possible. To date, no such exchange reactions are known in the field of polymers. Furthermore, no exchange reactions involving either hydrazones or imines are known when these functionalities comprise the polymeric backbone, i.e. fundamental repeating units of co-alternating polymers. A previous report has discussed co-alternating polymers involving the exchange concept applied to boronic acids and sugars, however the concept was only elucidated.

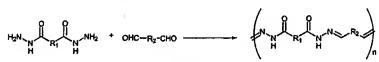
Scheme 4

Detailed Description of the Invention

The present invention relates to the novel application of alternating co-polymers, notably polyhydrazones and polyimines, but do not exclude others, where monomer units differing from those of the fundamental repeating units found in the polymeric backbone

can be exchanged. Polymers and oligomers are henceforth used interchangeably. The exchange reaction involves introducing the new difunctional monomer into the polymer at the expense of displacing a monomer unit constituting the alternating units of the polymer backbone. Difunctional monomers are of the type being of OHCRCHO, NH_2RNH_2, $NH_2NHC(O)RNHC(O)NH2$ where the radical group R may be, but is not limited to, aromatic (homo and hetero), aliphatic, conjugated, unconjugated, long alkyl chain, short alkyl chain, hydrophobic, hydrophilic, amphiphilic, or ionic in nature. The difunctional monomers comprising of aldehyde, carboxylic acid hydrazide, and amine functionalities, are henceforth referred to as dialdehydes, dihydrazides, and diamines, respectively. A dialdehyde or dihydrazide, or diamine, can be introduced into the polymer backbone. The incorporation results in the displacement of the monomer unit from the polymer yielding a free monomer. The end result is a new alternating co-polymer whose properties differ from those of the original polymer prior to monomer exchange. Some changes to the polymer physical properties that may occur upon exchanging monomers (i.e. Dynamerization) may include, but are not limited to the following: absorbance, fluorescence, solubility hydrophobicity, hydrophilicity (for a particular solvent), molecular weight, conductivity, T_g, castability, thermal stability, thermodynamic stability.

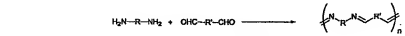
Polyhydrazones are readily prepared by those known in the art and subsequently isolated with ease. The polyhydrazones, represented by Scheme 5, are subsequently used as Dynamers, where a dihydrazide or dialdehyde may be incorporated into the polymeric backbone. Notable references for the synthesis of polyhydrazones are US patents 3 124 559, 4 158 014, 3 354 122 and JP 57 088 156. The monomers used for polyhydrazones polymerization were either aromatic, aliphatic, conjugated, hydrophobic, hydrophilic, amphiphilic, coloured, or colourless. The resulting polymers typically were conjugated, unconjugated, aliphatic, aromatic, short chain radical groups, long chain radical groups, hydrophobic, hydrophilic, amphiphilic, soluble in organic solvents known to those in the art. A few representative examples, but limited to these, are shown in Table 1.



Scheme 5

The present invention describes the polymerization involving the polycondensation of dialdehydes and diamines leading to polyimines, as depicted in Scheme 6, for the use of Dynamers. A few representative examples of typical polyimine synthesis are found in patents: WO 9504092, EP 0662486, US 3506613, GB 1320700, and 1080526. Some representative monomers used for polyimine synthesis were aromatic, aliphatic, conjugated, hydrophobic, hydrophilic, amphiphilic, coloured, colourless, or ionic. The resulting polymers typically were conjugated, unconjugated, aliphatic, aromatic, short chain radical groups, long chain radical groups, hydrophobic, hydrophilic, amphiphilic,

soluble in organic solvents known to those in the art, in addition to water. A brief list of monomer, but not limited to these, is found in Table 1.



Scheme 6

The alternating co-polymers of the type polyimines and polyhydrazones are exploited as Dynamers involving the exchange of the core repeating unit described in the following manner. The polymer solubility is not a crucial factor as monomer exchange progresses, the molecular weight of the original polymer decreases thereby increasing its solubility. Through the use of a volatile monomer, the equilibrium is shifted in favour of the new exchanged polymer leading to high molecular weight polymers, particularly where one stoichiometric equivalent is used. The solvents used for monomer exchange include DMSO, DMF, NMP, alcoholic solvents, and water, but are not limited to these. The catalyst used to promote monomer exchange was typically trifluoroacetic acid or acetic acid, but may also include others. Heating is required for exchanged to occur when using catalytic amounts of acid, however in some cases acid catalysis is not required. The heating temperature varies depending on the solvent selected and ranges from 50° to 150° C with an optimum value for practical purposes lying in the region of 70° to 95° C. The upper temperature limit is governed by the boiling point of the solvent selected for Dynamerization in addition of the thermal stability of the Dynamers. The reaction time for Dynamerization to occur varies according to the thermodynamic stability of the original and exchanged polymers, the amount of initial polymer, the amount of difunctional monomer added, the solvent, and the reaction temperature. Typically polyhydrazones and polyimines where found to optimally exchange with stoichiometric amounts of difunctional monomers at 75° C in DMSO with measured rate constants ca. 10^{-5} s^{-1}. The rates of exchange are accelerated with the addition of concentrated monomer.

Claims to the patent are as follows:

a) A polyhydrazone in a given compatible solvent when subjected to heat and/or acid catalysis in the presence of a dialdehyde results in a new polyhydrazone through the exchange of the dialdehyde monomer, as depicted in Scheme 7.

Scheme 7

b) A polyhydrazone in a given compatible solvent when subjected to heat and/or acid catalysis in the presence of a dihydrazide results in a new polyhydrazone through the exchange of the dihydrazide unit, as depicted in Scheme 8.

Scheme 8

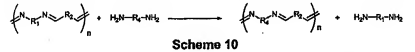
c) A polyhydrazone whose fundamental repeating units have been previously replaced by the Dynamerization process, in the presence of an excess of the originally displaced monomer (either dihydrazide or dialdehyde) along with acid catalysis and heat, the original polyimine can be regenerated.

The thermodynamic stability of the original polymer and the exchanged polymer upon monomer incorporation dictates the reaction conditions. With polyhydrazones comprising aryl radical groups, for exchange to occur with either an aryl or alkyl dihydrazide, a catalytic amount of trifluoroacetic acid, or other acid, is required in addition to heating. However, no catalyst is required for an aryl dihydrazide exchange of a dialkyl polyhydrazone. A catalyst is not required for introducing an aryl dialdehyde into an alkyl polyhydrazone. To effectively exchange an alkyl dialdehyde for one that is aryl when the dihydrazide group is aryl in nature, only the catalyst is required without the use of heat.

d) A polyimine in a given compatible solvent in the presence of a dialdehyde can undergo monomer dialdehyde exchange leading to a new polyimine with the use of mild heating and a catalyst, illustrated in Scheme 9.

Scheme 9

e) A polyimine in a given compatible solvent in the presence of a diamine can be exchanged giving rise to a new polyimine by exchanging the diamine monomers through the use of mild heating and the use of an acid catalyst, shown in Scheme 10.

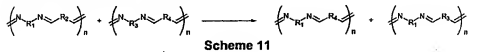


Scheme 10

f) A polyimine in a given compatible solvent in the presence of a dihydrazide can be exchanged leading to a new polyhydrazone by dihydrazide monomer exchange with mild heating and the use of an acid catalyst.

g) A polyimine can be depolymerised by acidifying the reaction medium then polymerized in the presence of a different monomer upon rendering the reaction medium alkaline leading to a new polyimine different than that at the onset of the depolymerization.

h) Two different polyimines in a given compatible solvent can exchange their fundamental repeating units by acid catalysis and heating resulting in two new polyimines, as depicted in Scheme 11.

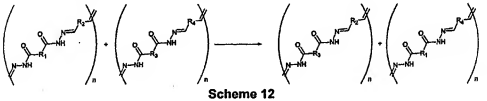


Scheme 11

i) A polyimine whose fundamental repeating units have been previously replaced by the Dynamerization process, in the presence of an excess of the originally displaced monomer (either diamine or dialdehyde) along with acid catalysis and heat, the original polyimine can be regenerated.

j) A polyimine in a given compatible solvent in the presence of a dihydrazide can undergo monomer exchange leading to a new polyhydrazone by replacing the diamine monomers with the dihydrazide through the use of mild heating and the use of an acid catalyst.

k) Two different polyhydrazones in a given compatible solvent can exchange their fundamental repeating units resulting in two new polyhydrazones, as depicted in Scheme 12, with the use of an acid catalyst and heat.

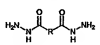
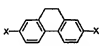
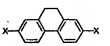
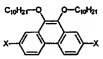
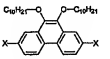
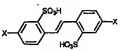
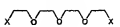
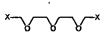


Scheme 12

l) A polyhydrazone and a polyimine in a given compatible solvent can exchange their fundamental repeating units resulting in a new polyhydrazone and a polyimine with the use of an acid catalyst and heat.

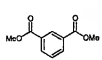
The present invention is illustrated by the following examples, which should not be taken in any way as imposing limitations upon the scope thereof. On the contrary, it is clear that various other embodiments, modifications, and equivalents thereof may suggest themselves to those skilled in the art after reading the description herein without departing from the spirit of the present invention and/or the scope of the claims hereafter.

Table 1

	Dihydrazide	Dialdehyde	Diamine
		OHC—R—CHO	H_2N—R—NH_2
Aromatic			
			
			
R=	1		
			
			
			
	$X-(CH_2)_8-X$	$X-(CH_2)_4-X$	$X-(CH_2)_4-X$
		$X-(CH_2)_3-X$	$X-(CH_2)_2-X$
Aliphatic		X–X	
R=			
			

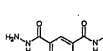
Having generally described the invention, the following examples serve to illustrate, but do not limit it in any way.

Monomer synthesis



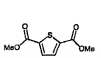
Isophthalic acid dimethyl ester

Isophthalic acid (5.45 g, 32.8 mmol) was dissolved in 175 ml methanol and refluxed for 18 hours after the addition of 15 ml of concentrated sulphuric acid. Half of the solvent volume was removed under reduced pressure then poured onto 250 ml iced water. The precipitate was filtered by vacuum filtration and washed with an abundant amount of water. The white solid was dried under vacuum where trace amounts of water were removed under diffusional reduced pressure to give 5.80 g (91 %) of product. M.p. 68° C. ^{1}H NMR (200 MHz, [D] chloroform): δ = 8.69 (s, 1 H), 8.23 (d, *J* = 7.8 Hz, 2 H), 8.09 (s, 1 H), 7.53 (t, *J* = 5.8 Hz, 2 H), 3.94 (s, 6 H). ^{13}C NMR (200 MHz, [D] chloroform): δ = 166.32, 133.86, 130.66, 128.67, 52.41. EI-MS: m/z 194.1 ([M]$^+$, 45%). Anal. calc. for $C_{10}H_{10}O_4$ (194.18): C 61.85, H 5.19, O 32.96 found: C 62.08, H 5.14.



Isophthalic acid dihydrazide

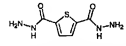
Isophthalic acid dimethyl ester (1.99 g, 10.3 mmol) was dissolved in 50 ml of absolute ethanol to which hydrazine monohydrate (4 ml, 81.9 mmol) was added. The solution was refluxed under argon for 2 hours. Upon cooling in an ice bath, a white precipitate formed and was filtered by vacuum filtration and further washed with cold absolute ethanol. The white crystalline solid was further dried under reduced pressure where 1.4 g (70 %) was collected. M.p. > 190° C. ^{1}H NMR (200 MHz, [D] DMSO): δ = 9.89 (b, s, 2 H), 8.26 (s, 1 H), 7.89 (d, *J* = 7.6 Hz, 4 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 4.31 (b, s, 4 H). ^{13}C NMR (200 MHz, [D] methanol): δ = 165.33, 133.45, 129.19, 128.27, 125.89. FAB-MS: m/z 195.3 ([M]$^+$, 100 %). Anal. calc. for $C_8H_{10}N_4O_2$ (194.19): C 49.48, H 5.19, N 28.85, O 16.48 found: C 50.62, H 6.06, N 27.07.



Thiophene-2,5-dicarboxylic acid dimethyl ester

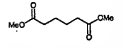
Thiophene-2,5-dicarboxylic acid (0.99 g, 5.7 mmol) was dissolved in 200 ml methanol and refluxed for 18 hours after the addition of 2 ml of concentrated sulphuric acid. Half of the solvent volume was removed under reduced pressure then poured onto 125 ml iced water. The white precipitate was filtered by vacuum filtration and washed with an abundant amount of water. The white solid was

dried under vacuum where trace amounts of water were removed under diffusional reduced pressure to yield 830 mg (75 %). M.p. 49° – 51° C. ^{1}H NMR (200 MHz, [D] chloroform): δ = 7.73 (s, 2 H), 3.91 (s, 6 H). ^{13}C NMR (200 MHz, [D] chloroform): δ = 190.62, 138.90, 133.13, 52.65. EI-MS: m/z 200.1 ([M]$^+$, 40%), 169.1 ([M-OCH$_3$]$^+$, 100%). Anal. calc. for $C_8H_8O_4S$ (200.2): C 47.99, H 4.03, O 31.96, S 16.02 found: C 47.29, H 3.79, S 16.24.



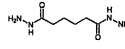
Thiophene-2,5-dicarboxylic acid dihydrazide

Thiophene-2,5-dicarboxylic acid dimethyl ester (830 g, 4.15 mmol) was dissolved in 100 ml of absolute ethanol to which hydrazine monohydrate (2.5 ml, 51.2 mmol) was added. The solution was refluxed under argon for 10 hours. Upon cooling in an ice bath, a white precipitate formed which was filtered by vacuum filtration and further washed with cold absolute ethanol. The yellow crystalline solid was further dried under reduced pressure. M.p. > 210° C. ^{1}H NMR (200 MHz, [D] DMSO): δ = 9.86 (s, 2 H), 4.50 (br, s, 4). FAB-MS: m/z 201.1 ([M]$^+$, 100%). Anal. calc. for $C_6H_8N_4O_2S$ (200.22): C 35.99, H 4.03, N 27.98, O 15.98, S 16.02 found: C 36.58, H 4.03, N 24.36, S 16.18.



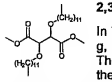
Hexanedioic acid dimethyl ester

Adipic acid (50.9 g, 345 mmol) was dissolved in 250 ml methanol and refluxed for 18 hours after the addition of 20 ml of concentrated sulphuric acid. The solution was cooled and the solvent was removed. To the yellow oil was added dichloromethane and washed with water. The organic layer was extracted and the solvent removed to give 52.3 g (87 %) of the product as a yellow oil. ^{1}H NMR (200 MHz, [D] chloroform): δ = 3.64 (s, 6 H), 2.32 (t, 4 H), 1.64 (t, 6 H). EI-MS: m/z 174.1 ([M]$^+$, 20%), 143.1 ([M-OCH$_3$]$^+$, 80%). Anal. calc. for $C_8H_{14}O_4$ (174.1): C 55.1, H 8.10, O 36.74 found: C 54.33, H 8.35.



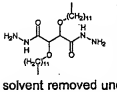
Hexanedioic acid dihydrazide

Hexanedioic acid dimethyl ester (5.74 g, 32.9 mmol) was dissolved in 100 ml of absolute ethanol to which hydrazine monohydrate (4 ml, 81.9 mmol) was added. The solution was stirred at room temperature for twelve hours then refluxed under argon for 4 hours. The majority of the solvent was removed under reduced pressure where a white precipitate eventually formed. The precipitate was filtered by vacuum filtration and further washed with cold absolute ethanol. The white crystalline solid was further dried under reduced pressure. M.p. > 200 °C. ^{1}H NMR (200 MHz, [D] DMSO): δ = 8.90 (s, 2 H), 4.41 (s, 4 H), 1.99 (s, 4 H), 1.44 (s, 4 H). FAB-MS: m/z 175.2 ([M]$^+$, 100%). Anal. calc. for $C_6H_{14}N_4O_2$ (174.20): C 41.37, H 8.10, N 32.16, N 18.37 found: C 41.88, H 31.55 , N 18.39.



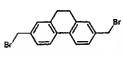
2,3-Bis-dodecyloxy-succinic acid dimethyl ester

In 75 ml methanol was dissolved 2,3-bis-dodecyloxy-succinic acid (1.15 g, 2.36) to which 15 drops of concentrated sulphuric acid was added. The mixture was refluxed was 12 hours then solvent was removed and the oil was poured onto 200 ml ice water. The product was isolated as a white solid (1.12 g, 92 %) after filtering the resulting precipitate. M.p. 48° C. ^{1}H NMR (200 MHz, [D] DMSO): δ = 4.42 (s, 2 H), 3.65 (s, 8 H), 3.31 (q, 2 H), 1.43 (m, 4 H), 1.14 (m, 36 H), 0.79 (t, 6 H). ^{13}C δ = 169.99, 92.41, 90.18, 82.17, 73.34, 72.72, 33.08, 30.99, 30.79, 30.69, 30.45, 27.30, 23.81, 15.56. FAB-MS: m/z 515.5 ([M]$^+$, 100%). Anal. calc. for $C_{30}H_{58}O_6$ (514.78): C 70.00, H 11.36, O 18.65 found: C 69.72, H 11.73.



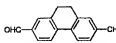
2,3-Bis-dodecyloxy-succinic acid dihydrazide

In 100 ml absolute ethanol was added 2,3-bis-dodecyloxy-succinic acid dimethyl ester (6.22 mg, 1.21 mmol) followed by hydrazine hydrate (1.5 ml, 4.82 mmol) and the solution was refluxed for 12 hours under argon. The solution was cooled and most of the solvent removed under reduced pressure till a precipitate formed that was subsequently filtered and washed with water. The resulting white solid was dried under vacuum yielding 565 mg (91 %) of the product. M.p. > 200° C. ^{1}H NMR (200 MHz, [D] DMSO): δ = 8.62 (s, 2 H), 4.02 (s, 2 H), 3.48 (t, 2 H), 3.31 (t, 2 H), 3.07 (t, 2 H), 1.46 (t, 4 H), 1.25 (m, 42 H), 0.86 (t, 6 H). ^{13}C NMR (200 MHz, [D] chloroform): δ = 169.99, 92.41, 90.18, 82.17, 73.34, 72.72, 33.08, 30.99, 30.79, 30.69, 30.45, 27.30, 23.81, 15.56. FAB-MS: m/z 515.4 ([M]$^+$, 100%). Anal. calc. for $C_{28}H_{58}N_4O_4$ (514.78): C 65.33, H 11.36, N 10.88, O 12.43 found: C 64.69, H 11.31, N 10.70.



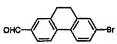
2,7-Bis-bromomethyl-9,10-dihydro-phenanthrene

9,10-Dihydro-phenanthrene (40.25 g, 223 mmol) was dissolved in 100 ml anhydrous THF followed by solid paraformaldehyde (30.93 g), concentrated hydrobromic acid (80 ml) and 30 % hydrobromic acid in acetic acid (90 ml). The slurry was heated to 80 °C under argon where the yellow colour was eventually replaced by an orange one. After 19 hours, the temperature was raised to 120° C for a gentle reflux to produce a red colour. The solution was cooled in an ice bath after 7 hours and the precipitate formed was filtered off. The beige solid was taken up into 300 ml acetone and physically broken up with a spatula and by sonication. The slurry was heated lightly then cooled and the precipitate filtered to give 30.4 g (38 %) of the product as an off white solid. M.p. 158° - 162° C. ^{1}H NMR (200 MHz, [D] chloroform): δ = 7.72 (d, *J* = 7.7 Hz, 2 H), 7.34 (d, *J* = 7.7 Hz, 2 H), 7.28 (s, 2 H), 4.52 (s, 4 H), 2.86 (s, 4 H). ^{13}C NMR (200 MHz, [D] chloroform): δ = 138.03, 137.16, 134.29, 128.96, 127.84, 124.30, 33.63, 28.89. EI-MS: m/z 363.9 ([M]$^+$, 10%), 284.9 ([M]$^+$-Br, 100%). Anal. calc. for $C_{16}H_{14}Br_2$ (363.95): C 52.49, H 3.85, Br 43.65 found: C 52.73, H 43.80.

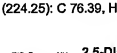


9,10-Dihydro-phenanthrene-2,7-dicarbaldehyde

2,7-Bis-bromomethyl-9,10-dihydro-phenanthrene (7.07 g, 19.3 mmol) was dissolved in 100 ml DMSO along with sodium hydrogen carbonate (26.96 g, 321 mmol). The solution was heated to 115° C under argon where the colour eventually becomes lemon yellow. The solution is eventually cooled after 6 hours of heating and poured onto water. The solid is removed through filtering and then dissolved in dichloromethane. After removal of the solvent, the crude product is purified by flash chromatography with dichloromethane to give 1.2 g (26 %) of the title compound as a yellow solid. M.p. 172° – 174° C. ^{1}H NMR (200 MHz, [D] chloroform): δ = 10.01 (s, 2 H), 7.95 (d, *J* = 7.7, Hz, 2 H), 7.83 (d, *J* = 7.7 Hz, 2 H), 7.77 (s, 2 H), 2.97 (s, 4 H). ^{13}C NMR (200 MHz, [D] chloroform): δ = 191.84, 139.15, 138.91, 136.19, 129.35, 128.91, 125.28, 28.59. EI-MS: m/z 236.1 ([M]$^+$, 100%). Anal. calc. for $C_{16}H_{12}O_2$ (236.27): C 81.34, H 5.12, O 13.54 found: C 80.17, H 4.86.



Isolated (540 mg, 9 %) as lime green solid from the 9,10-dihydro-phenanthrene-2,7-dicarbaldehyde reaction mixture. M.p. 109° – 112° C.; ^{1}H NMR (200 MHz, [D] chloroform): δ = 10.01 (s, 2 H), 7.95 (d, *J* = 7.7 Hz, 2 H), 7.83 (d, *J* = 7.7 Hz, 2 H), 7.77 (s, 2 H), 2.97 (s, 4 H). ^{13}C NMR (200 MHz, [D] chloroform): δ = 191.88, 140.31, 139.34, 138.91, 136.12, 132.16, 129.20, 128.91, 127.85, 124.79, 124.16, 38.19, 28.59. EI-MS: m/z 221.1 ([M-Br]$^+$, 100%).



Isolated (300 mg, 1 %) as lemon yellow solid from 9,10-dihydro-phenanthrene-2,7-dicarbaldehyde reaction mixture. M.p. 116° – 118° C. ^{1}H NMR (200 MHz, [D] chloroform): δ = 9.88 (s, 1 H), 7.74 (s, *J* = 7.7, Hz, 4 H), 7.72 (d, *J* = 7.7, Hz, 2 H), 7.21 (s, 2 H), 4.67 (s, 2 H), 2.82 (s, 4 H). ^{13}C NMR (200 MHz, [D] chloroform): δ = 192.25, 142.03, 140.48, 138.44, 138.44, 138.00, 135.09, 132.56, 129.31, 128.93, 126.99, 125.83, 124.85, 124.22, 64.8, 28.83. EI-MS: m/z 238.1 ([M]$^+$, 100%). Anal. calc. for $C_{16}H_{12}O_2$ (224.25): C 76.39, H 5.74, O 14,27 found: C 76.53, H 5.62.

2,5-Diamino-thiophene-3,4-dicarboxylic acid diethyl ester

Solid elemental sulphur (19.24 g, 0.6 mol) was charged into a 2 necked round bottom flask followed by 100 ml DMF. To the yellow slurry, was added triethylamine (30 ml, 0.21 mol) where the colour immediately turned copper like. This slurry was allowed to mix at room temperature for 75 minutes after which ethyl cyanoacetate (85 ml, 0.79 mol) was added drop wise. The slurry was allowed to stir at room temperature for several days then eventually poured onto 200 g ice where a precipitate immediately formed. Residual sulphur was digested with 200 ml carbon disulfide and the product recrystalized twice from ethanol. The crude yellow

product was then chromatographed on silica with 40 % ethyl acetate/hexane to afford the product as a yellow like solid (11.27 g, 41 %). M.p. 155° – 158° C. ^{1}H NMR (200 MHz, [D] chloroform): δ = 5.28 (br, s, 4 H), 4.42 (q, 4 H), 1.28 (t, 6 H). ^{13}C NMR (200 MHz, [D] chloroform): δ = 165.25, 148.71, 60.11, 14.42. EI-MS: m/z 258.1 ([M]$^+$, 80%), 212 ([M-C2H5O]$^+$, 100%). Anal. calc. for $C_{10}H_{14}N_2O_4S$ (258.30): C 46.50, H 5.46, N 10.85, O 24.78, S 12.41 found: C 45.89, H 5.10, N 10.47, S 12.01.

3,4-Bis-decyl-thiophene

In 100 ml anhydrous THF was dissolved 3,4-dibromothiophene (4.89 g, 20 mmol) and cooled to 0° C under an argon atmosphere to which was then added [1,3-bis(diphenylphosphino)propane]nickel (II) chloride (196 mmol, 0.38 mmol). To the red coloured solution was then added decylmagnesium bromide (45 ml, 45 mmol) then the brown solution was refluxed for 12 hours then stirred at room temperature for 14 hours. The solution was passed through a plug of celite and silica then chromatographed on silica with 100% hexane to afford the title compound as a colourless oil (4.96 g, 80%). ^{1}H NMR (200 MHz, [D] chloroform): δ = 6.95 (s, 2 H), 6.96 (d, *J* = 8.2, 2 H), 2.69 (t, 4 H), 1.71 (t, 4 H), 1.37 (m, 34 H), 0.98 (t, 6 H). ^{13}C NMR (200 MHz, [D] chloroform): δ =141.11, 120.03, 32.95, 32.13, 30.76, 30.48, 30.23, 29.84, 29.56, 29.02, 22.86, 14.27. EI-MS: m/z 364.5 ([M]$^+$, 100 %). Anal. calc. for $C_{24}H_{44}S$ (364.32): C 79.05, H 12.16, S 8.79 found: C , H , S .

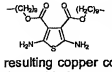
3,4-Bis-decyl-thiophene-2,5-dicarbaldehyde

The oil of 3,4-bis-decyl-thiophene (1.4 g, 3.85 mmol) was diluted in 16 ml anhydrous hexane then cooled to –70° C under an argon atmosphere. To this was added TMEDA (1.3 ml, 8.47 mmol) followed by 0.5 M solution *n*-butyl lithium (4.2 ml, 8.47 mmol) in hexane. The reaction mixture was allowed to warm to room temperature then refluxed. After 90 minutes, the reaction mixture was cooled to 0° C to which was then added 10 ml anhydrous DMF and then allowed to warm to room temperature and further react for 30 minutes. Aqueous 2M HCl was then added to quench the reaction. The organic layer was extracted with ethyl acetate, the solvent removed under reduced pressure, then the oil purified by flash chromatography. The product was isolated as a colourless oil (40 %). ^{1}H NMR (200 MHz, [D] chloroform): δ = 10.12 (2 H), 2.69 (t, 4 H), 1.71 (t, 4 H), 1.37 (m, 34 H), 0.98 (t, 6 H). ^{13}C NMR (200 MHz, [D] chloroform): δ = 183.7, 151.6, 143.11, 32.95, 32.13, 30.76, 30.48, 30.23, 29.84, 29.56, 29.02, 22.86, 14.27. EI-MS: m/z 420.69 ([M]$^+$, 100 %).

Cyano-acetic acid decyl ester

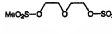
Into a 100 ml round bottom flask was charged cyanoacetic acid (20.85 g, 0.24 mol), methane sulfonic acid (0.5 ml, 7.8 mmol), and decanol (47 ml, 0.25 mol). The reaction mixture was heated under reduced pressure and the water removed by azeotrope distillation through the use of a Dean-Stark

apparatus. The reaction temperature was kept below 150° C and eventually cooled upon formation of theoretical amount of water. The reaction goes to completion and purification is not required. ^{1}H NMR (200 MHz, [D] chloroform): δ = 4.10 (t, 2 H), 3.41 (s, 2 H), 1.57 (m, 2 H), 1.18 (m, 15 H), 0.80 (m, 3 H). ^{13}C NMR (200 MHz, [D] chloroform): δ = 163.31, 113.39, 66.86, 31.89, 29.51, 29.26, 29.17, 28.34, 25.67, 24.65, 22.67, 14.03. EI-MS: m/z 226.3 ([M]$^+$, 55 %).



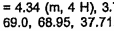
2,5-Diamino-thiophene-3,4-dicarboxylic acid didecyl ester

In a 250 ml round bottom flask was charged sulfur flower (5.80g, 0.18 mol) followed by 100 ml DMF and 40 ml triethylamine. The resulting copper colour slurry was stirred at room temperature for 1 hour to which was then added cyano-acetic acid decyl ester (0.24 mol). The deep dark red solution was stirred for 4 days at room temperature then poured onto 800 ml absolute ethanol. The unreacted sulfur (1.73 g, 0.05 mmol) was filtered off and the solvent removed to yield a deep red oil that was chromatographed on silica (15 % ethyl acetate / 85 % hexane) to yield the title compound as a yellow oil. ^{1}H NMR (200 MHz, [D] chloroform): δ = 5.3 (br, s, 4 H), 4.0 (t, 2 H), 1.6 (m, 2 H), 1.2 (m, 15 H), 0.8 (m, 3 H). ^{13}C NMR (200 MHz, [D] chloroform): δ = 165.3, 148.71, 66.8, 31.7, 29.5, 29.26, 29.2, 28.3, 25.8, 24.6, 14.0. EI-MS: m/z 482.3.3 ([M]$^+$, 55 %).



Methanesulfonic acid 2-(2-methanesulfonyloxy-ethoxy)-ethyl ester

Diethylene diglycol (10ml, 105 mmol) diluted in 150 ml anhydrous THF cooled to 0° C to which anhydrous triethylamine (37 ml, 300 mmol) was added. Methanesulfonyl chloride (28 ml, 362 mmol) was diluted in 50 ml anhydrous THF and added dropwise to the glycol solution. After complete addition, the reaction slurry was stirred for 30 minutes at 0° C then allowed to warm to room temperature where the reaction mixture was subsequently allowed to stir for 4 hours. The mixture was then poured onto 150 ml brine saturated ice water. The organic layer was extracted with dichloromethane and the solvent removed to give the product as a white solid (19.9 g, 73 %). ^{1}H NMR (200 MHz, [D] chloroform): δ = 4.34 (m, 4 H), 3.76 (m, 4 H), 4.66 (s, 4 H). ^{13}C NMR (200 MHz, [D] chloroform): δ = 69.0, 68.95, 37.71, 31.68. EI-MS: m/z 166.2 ([M-SO_3CH_3]$^+$, 80 %). Anal. calc. for $C_6H_{14}O_7S_2$ (262.30): C 27.47, H 5.38, O 42.70, S 24.45 found: C 27.68, H 5.42 , S 24.57.



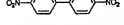
1-Azido-2-(2-azido-ethoxy)-ethane

Methanesulfonic acid 2-(2-methanesulfonyloxy-ethoxy)-ethyl ester (14.02 g, 53.4 mmol) was dissolved in 100 ml anhydrous THF to which sodium azide (7.35 g, 113 mmol) was added. The slurry was refluxed under argon for approximately 14 hours till all the starting material was judged consumed by TLC. The solvent was removed under reduced pressure. The resulting white solid was taken up in dichloromethane and then

passed through a plug of silica gel. The product was isolated as a yellow-green liquid (6.39 g, 77 %). ^{1}H NMR (200 MHz, [D] chloroform): δ = 3.64 (m, 4 H), 3.34 (m, 4 H). ^{13}C NMR (200 MHz, [D] chloroform): δ = 70.07, 50.80. EI-MS: m/z 71.4 ([M-6N]$^+$, 100 %). Anal. calc. for $C_4H_8N_6O$ (156,15): C 32.16, H 5.84, N 47.76. found: C 31.16, H 5.10, N 47.11.

2-(2-Amino-ethoxy)-ethylamine

1-Azido-2-(2-azido-ethoxy)-ethane (7 g, 44.9 mmol) was diluted in 100 ml anhydrous THF followed by triphenyl phosphine (25 g, 95.3 mmol) and water (1.7 ml, 94.4 mmol) then refluxed for 12 hours. The solvent was removed then dichloromethane was added. 2M HCl was added till the aqueous layer was acid. The organic layer was removed and potassium carbonate was added to the aqueous layer till alkaline. To this layer was added dichloromethane and the organic layer extracted. The product was isolated as a colourless oil (3 g, 64 %) upon removing the dichloromethane under reduced pressure. ^{1}H NMR (200 MHz, [D] chloroform): δ = 3.14 (m, 4 H), 2.52 (m, 4 H), 1.00 (m, 4). ^{13}C NMR (200 MHz, [D] chloroform): δ =73.02, 41.69. EI-MS: m/z 105.4 ([M]$^+$, 30 %). Anal. calc. for $C_4H_{12}N_2O$ (104.09): C 46.13, H 11.61, N 26.90, O 15.36 found: C 36.68, H 10.67, N 19.40.



2,7-Dinitro-9,10-dihydro-phenanthrene

9,10-dihydro-phenanthrene (3.03 g, 11.2 mmol) was dissolved in 30 ml concentrated acetic acid and warmed to 50° C to which fuming nitric acid (20 ml) was added dropwise. The resulting red solution was heated to 50° C for 2 hours then cooled and poured onto 300 ml ice water. The precipitate was removed under vacuum filtration, washed with an abundant amount of water, the dried under vacuum.. The product was isolated as a bright yellow solid. M.p. 198° - 208° C. ^{1}H NMR (200 MHz, [D] DMSO): δ = 8.21 (s, 2 H), 8.15 (d, *J* = 2.1, 2 H), 7.89 (d, *J* = 8.2, 2H), 2.99 (s, 4 H). ^{13}C NMR (200 MHz, [D] chloroform): δ = 147.88, 139.49, 138.62, 125.66, 123.53, 122.65, 30.96. EI-MS: m/z 270.0 ([M]$^+$, 100 %). Anal. calc. for $C_{14}H_{10}N_2O_4$ (270.24): C 62.22, H 3.73, N 10.37, O 23.68 found: C 61.59, H 3.54, N 10.71.

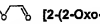
9,10-Dihydro-phenanthrene-2,7-diamine

2,7-Dinitro-9,10-dihydro-phenanthrene (3.03 g, 11.2 mmol) was dissolved in 30 ml concentrated acetic acid and warmed to 50° C to which a solution of stannous chloride (17.5g, 78 mmol) dissolved in 50 ml concentrated hydrochloric acid previously heated to 50° C was added dropwise. The resulting red solution was heated to 50° C for 20 minutes then the solvent removed under reduced pressure. An aqueous solution of 50 % sodium hydroxide was added to the oil that caused a precipitate. The precipitate was washed with copious amounts of sodium hydroxide and water then chromatographed with 5 % methanol/dichloromethane

to afford the title compound as a beige/brown solid (1.67 g, 71 %) which decomposes upon exposure to ambient light. M.p. 144° - 148° C. ^{1}H NMR (200 MHz, [D] chloroform): δ = 7.42 (d, *J* = 8.2, 2 H), 6.96 (d, *J* = 8.2, 2 H), 6.54 (d, *J* = 8.2, 2 H), 3.61 (s, 4 H), 2.74 (s, 4 H). ^{13}C NMR (200 MHz, [D] chloroform): δ =137.69, 123.82, 114.79, 113.83, 29.51. FAB-MS: m/z 209.8 ([M]$^+$, 100 %). Anal. calc. for $C_{14}H_{14}N_2$ (210,27): C 79.7, H 6.71, N 13.32 found: C 79.37, H 6.51, N 13.19.

{2-[2-(2-Oxo-ethoxy)-ethoxy]-ethoxy}-acetaldehyde

Typical Swern oxidation procedure was employed. Dichloromethane, 40 ml, was cooled to –55° C with the use of an isopropanol/dry ice bath to which was added anhydrous oxalyl chloride (2.5 ml, 28.7 mmol) under an argon atmosphere. To this solution was added dropwise over a period of 5 minutes a solution of anhydrous DMSO (4 ml, 56.99 mmol) diluted in 5 ml dichloromethane. After complete addition of DMSO, tetraethylene glycol (2.4 ml, 13.8 mmol) was added dropwise. The reaction mixture was allowed to stir for 30 minutes at –50° C before adding anhydrous triethylamine (20 ml, 143.6 mmol) where upon addition a white slurry formed. The temperature was allowed to warm to 0° C where the precipitate was filtered off. The resulting filtrate was washed twice with 20 ml water and extracted. The water from the aqueous layer was removed under reduced pressure and the product used without further purification for immediate polymerization in the presence of diamines.



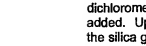
[2-(2-Oxo-ethoxy)-ethoxy]-acetaldehyde

Triethylene glycol (1 ml, 7.49 mmol) was diluted with 150 ml dichloromethane and cooled to 0° C. To this was added trichloroisocyanuric acid (3.49 g, 15.0 mmol) followed by a catalytic amount of 2,2,6,6-tetramethylpiperidine-N-oxide (TEMPO). The heterogeneous solution immediately becomes orange then the colour dissipates. After 20 minutes, the reaction mixture is poured over a plug of celite and the solvent removed under vacuum. The title compound was isolated as a colourless oil (900 mg, 80 %) then kept over 20 ml water with a trace amount of trifluoroacetic acid to avoid autopolymerization. ^{1}H NMR (200 MHz, [D] chloroform): δ = 9.46 (s, 2 H), 3.71 (s, 8 H). ^{13}C NMR (200 MHz, [D] chloroform): δ =200.33, 71.18, 30.91.

(2-Oxo-ethoxy)-acetaldehyde

Diethylene glycol (2 g, 19.6 mmol) was diluted in dichloromethane to which was added 1,3,5-trichloro-2,4,6-triazinetrione (trichloroisocyanuric acid; 9.2 g, 39.2 mmol) and a catalytic amount of TEMPO, all at 0° C The reaction mixture was allowed to warm to room temperature and stirred for approximately 45 minutes till the starting alcohol was consumed as determined by TLC then filtered through Celite. The organic layer was washed with saturated sodium carbonate then extracted with dichloromethane. The title

compound was isolated as a colourless oil upon removal of the solvent under reduced pressure. ^{1}H NMR (200 MHz, [D] chloroform): δ = 9.72 (2 H), 4.48 (4 H). ^{13}C NMR (200 MHz, [D] chloroform): δ =200.1, 83.3.



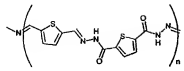
Hexanedial

Sodium metaperiodate (2.61 g, 12.2 mmol) was dissolved in 5 ml water that was heated until complete dissolution. Fine mesh silica gel was then added to give a slurry then a further small quantity was added to give a gel. To this was added 50 ml dichloromethane and vigorously shaken. Cyclohexandiol (522 mg, 4.49 mmol) was then added. Upon complete diol formation as determined by TLC usually under 30 minutes, the silica gel was removed by filtration and further washed with 100 ml dichloromethane. The solvent was then removed under reduced pressure to give the title compound as a yellow oil that was immediately used without further purification. . ^{1}H NMR (200 MHz, [D] chloroform): δ =. 9.45 (s, 2H), 2.18 (m, 4H), 1.35 (m, 4H). ^{13}C NMR (200 MHz, [D] chloroform): δ = 201.83, 43.24, 21.26.

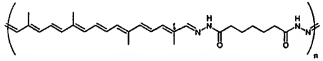
General method of polyhydrazone synthesis

Typically between 100 and 200 mg of dihydrazide monomer was added to between 250 and 350 ml absolute ethanol. The heterogeneous solution is rendered homogenous by heating the reaction mixture for 15 minutes followed by placing it in an ultrasonic bath for approximately 15 minutes. Complete dissolution is achieved by repeating the above process once or twice more. While the homogeneous solution is still warm, a stoichiometric amount of dialdehyde is added where the medium immediately becomes troubled. The addition of a catalyst in the form of acid is not required, but drastically decreases the reaction time. Acid catalysts may be hydrochloric acid, acetic acid, or trifluoroacetic acid where between 2 and 10 drops are sufficient to promote polymerization ensuing precipitation. The polymeric slurry is stirred at room temperature varying from 3 to 12 hours where the desired polymer is obtained by filtration. The polymer isolated in the form of a cake and was washed with an abundant amount of water then dried under vacuum.

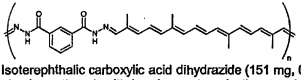
Alternatively, approximately 150 mg of dihydrazide is taken up between 50 and 75 ml of DMSO (methyl sulfoxide) and then placed in an ultrasound bath for 15 minutes to ensure complete dissolution. While the solution is homogenous, one stoichiometric equivalent of the desired dialdehyde is added followed by 3 drops of either acetic acid or trifluoroacetic acid. The resulting polymers precipitate immediately upon acid addition. The polymerization was allowed to proceed at room temperature for four hours then the polymer was isolated by suction filtration, then washed with an abundant amount of water and dried under vacuum to give typically a white solid.



2,5-Thiophene dicarboxylic acid dihydrazide (82.1 mg, 0.41 mmol) was dissolved in 250 ml absolute ethanol upon heating and sonicating for 30 minutes. To this solution was added 2,5-thiophene dicarboxaldehyde (38.2 mg, 0.41 mmol) followed by ten drops of concentrated acetic acid immediately inducing the precipitation of the orange polymer. The heterogeneous solution was further stirred for 5 hours at room temperature then the precipitate was isolated by filtering and subsequently washed with water followed by drying under vacuum. The polymer was isolated as an orange powder upon drying (80 g, 76 %) and was slightly soluble in DMSO and DMF. DP = 25, MW = 5913. ^{1}H NMR (200 MHz, [D] DMSO): δ = 11.54 (s, 1 H), 11.07 (s, 1 H), 7.13 (br, s, 6 H). Anal. calc. for $C_{12}H_8N_4S_2$ x 1.5 H_2O: C 48.15, H 3.70, S 21.42 found: C 43.78, H 3.31, N 15.89, S 25.78.

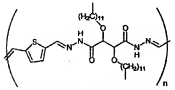


Adipic carboxylic acid dihydrazide (170 mg, 0.97 mmol) was dissolved in 400 ml absolute ethanol, with heating and sonication, to which was added crocetin dialdehyde (289 mg, 0.97 mmol). When the solution cooled to room temperature, five drops of concentrated acetic acid was added. The heterogeneous solution was stirred for 24 hours at room temperature where the resulting red polymer was isolated by filtration then dried under vacuum. The polymer was isolated as a deep red solid (214 mg, 51 %) and was lightly soluble in DMSO and DMF, NMP. Anal. calc. for $C_{26}H_{34}N_4O_2$ x 5.95 H_2O: C 57.64, H 8.54, N 10.34 found: C 55.32, H 6.16, N 9.57.

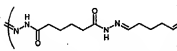


Isoterephthalic carboxylic acid dihydrazide (151 mg, 0.78 mmol) was dissolved in 500 ml absolute ethanol, with heating and sonication, to which was added crocetin dialdehyde (231 mg, 0.94 mmol). When the solution cooled to room temperature, five drops of concentrated acetic acid was added. The heterogeneous solution was stirred for 24 hours at room temperature where the resulting red polymer was isolated by filtration then dried under vacuum. The polymer was isolated as a deep red solid (200 mg, 57 %) lightly soluble in DMSO and DMF, NMP. ^{1}H NMR (200 MHz, [D] DMSO): δ = 11.73 (br, s, 2 H), 8.36 (br, s, 2 H), 8.07 (br, s, 1 H), 7.86 (br, s, 2 H), 6.09 (br, s, 10 H), 2.06 (br, s,

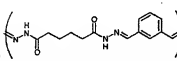
6 H), 1.24 (br, s, 6 H). Anal. calc. for $C_{28}H_{30}N_4O_2$ x 4.65 H_2O: C 62.47, H 7.36, N 10.11 found: C 61.13, H 5.97, N 9.05.



2,3-Bis-dodecyloxy-succinic acid dihydrazide (80 mg, 0.15 mmol) was dissolved in 50 ml absolute ethanol to which was added 2,5-thiophene dicarboxaldehyde (24 mg, 0.17 mmol) followed by a few drops of concentrated acetic acid immediately. The homogeneous solution was stirred for 2 days at room temperature then the solvent removed under reduced pressure followed by drying under vacuum. The polymer was isolated as a yellow-green coloured solid (80 mg, 81 %) soluble in DMSO, DMF, NMP, ethanol, dichloromethane, chloroform, and acetonitrile. DP = 9, MW = 5562. ^1H NMR (200 MHz, [D] $CDCl_3$): δ = 9.63 (br, s, 1 H), 8.84 (br, s, 1 H), 7.69 (br, s, 2 H), 7.40 (br, s, 2 H), 4.44 (br, s, 2 H), 3.63 (br, s, 4 H), 1.25 (br, s, 46 H). Anal. calc. for $C_{34}H_{58}N_4SO_4$ x 1.25 H_2O: C 63.87, H 9.51, N 8.73, S 5.00 found: C 64.17, H 8.87, N 8.10, S 4.77.

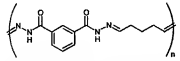


Adipic acid dihydrazide (1.49 g, 8.55 mmol) was dissolved in 500 ml absolute ethanol upon heating and sonicating for 30 minutes. To this solution was added 50 % aqueous solution of glutaric dialdehyde (8.04 ml, 8.55 mmol) followed by a ten drops of concentrated acetic acid immediately inducing the precipitation of the polymer. The heterogeneous solution was further stirred for 5 hours at room temperature then the precipitate was isolated by filtering and subsequently washed with water followed by drying under vacuum. The polymer was isolated as a rubbery latex that becomes crystalline upon drying (1.13 g, 87 %) and slightly soluble in DMSO, NMP, and DMF. DP = 25, MW = 5913. ^1H NMR (200 MHz, [D] DMSO): δ = 10.89 (s, 1 H), 10.74 (s, 1 H), 7.46 (s, 1 H), 7.08 (s, 1 H), 2.19 (br, s, 8 H), 1.53 (br, s, 6 H). Anal. calc. for $C_{11}H_{18}O_2N_4$ x 0.4 H_2O: C 53.82, H 7.72, N 22.82 found: C 54.14, H 6.70, N 21.87.

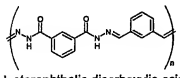


Adipic acid dihydrazide (1.01 g, 5.79 mmol) was dissolved in 250 ml absolute ethanol upon heating and sonicating for 20 minutes. To this solution was added Isoterephthalic dicarboxaldehyde (0.78 g, 5.81 mmol) followed by a couple of drops of concentrated hydrochloric acid that immediately induced the precipitation of the polymer. The heterogeneous solution was further stirred for 5 hours at room temperature then the

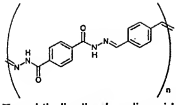
precipitate was isolated by filtering and subsequently washed with water followed by drying under vacuum. The polymer was isolated as a white solid (1.13 g, 72%) slightly soluble in DMSO and DMF, NMP. DP = 15, MW = 4080. ^{1}H NMR (200 MHz, [D] DMSO): δ = 11.43 (s, 1 H), 11.27 (s, 1 H), 7.99 (m, 3 H), 7.64 (m, 3 H), 2.67 (m, 4 H), 2.23 (m, 2 H), 1.66 (m, 2 H). Anal. calc. for $C_{14}H_{20}N_4O_2$ x H_2O: C 60.07, H 7.35, N 20.01 found: C 58.65, H 5.92, N 19.80.



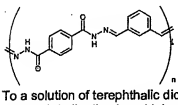
Isoterephthalic carboxylic acid dihydrazide (165 g, 0.85 mmol) was dissolved in 100 ml absolute ethanol upon heating and sonicating for 20 minutes. To this solution was added 50 % aqueous solution of glutaric dialdehyde (200 µl, 0.85 mmol) followed by a couple of drops of concentrated acetic acid that immediately induced the precipitation of the polymer. The heterogeneous solution was further stirred for 5 hours at room temperature then the precipitate was isolated by filtering and subsequently washed with water followed by drying under vacuum. The polymer was isolated as a white solid (113 mg, 55%) slightly soluble in DMSO, NMP, and DMF. DP = 18, MW = 4644. ^{1}H NMR (200 MHz, [D] DMSO): δ = 11.59 (s, 2 H), 8.32 (br, s, 1 H), 7.99 (d, 2 H), 7.79 (s, 2 H), 7.60 (t, 1 H), 2.35 (br, s, 4 H), 1.76 (br, s, 2 H). Anal. calc. for $C_{13}H_{14}N_4O_2$ x 0.65 H_2O: C 57.83, H 5.71, N 20.75 found: C 57.75, H 4.59, N 19.65.



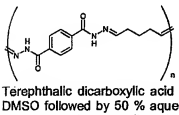
Isoterephthalic dicarboxylic acid hydrazide (40 mg, 0.21 mmol) was dissolved in 200 ml absolute ethanol with heating and sonicating. To this was added isoterephthalic dicarboxaldehye (27.6 mg, 0.21 mmol) was added once the ethanol solution had cooled followed by a trace amount of acetic acid. Immediately a white precipitate forms and then was allowed to stir at room temperature over night. The precipitate was filtered, washed with water and dried under vacuum to give the polymer as a white solid (52 mg, 82 %) slightly soluble in DMSO and DMF. DP = 23, MW = 6716. ^{1}H NMR (200 MHz, [D] DMSO): δ = 12.13 (s, 2 H), 8.56 (m, 2 H), 8.49 (m, 3 H), 8.17 (m, 3 H), 8.13 (m, 2 H), 7.78 (m, 2 H), 7.56 (m, 2 H). Anal. calc. for $C_{16}H_{12}N_4O_2$ x $1H_20$: C 61.93, H 4.55, N 19.17 found: C 61.97, H 4.62, N 18.76.



Terephthalic dicarboxylic acid hydrazide (175 mg, 0.90 mmol) was dissolved in 70 ml DMSO upon submerging the flask in an ultrasound bath for 25 minutes. To this solution was then added terephthalic dicarboxaldehyde (122 mg, 0.91 mmol) and the solution was allowed to stir at room temperature for 18 hours. The resulting yellow/green precipitate was isolated by vacuum filtration, washed with an abundant amount of water then dried under vacuum to give 232 mg (83 %) of the polymer which is only slightly soluble in DMSO and NMP. ^{1}H NMR (200 MHz, [D] DMSO): δ = 12.04 (s, 2 H), 8.46 (br, s, 2 H), 8.11 (br, s, 2 H), 7.96 (br, s, 2 H) 7.79 (br, s, 2 H). Anal. calc. for $C_{16}H_{12}N_4O_2$ x 1.95 DMSO x 0.05 H_2O: C 53.65, H 5.38, N 12.57 found: : C 53.31, H 5.04, N 12.90.



To a solution of terephthalic dicarboxylic acid hydrazide (165 mg, 0.85 mmol) was added isoterephthalic dicarboxaldehyde (114 mg, 0.85 mmol) and the mixture was allowed to stir at room temperature for 18 hours. The polymer was isolated as a yellow solid (255 mg, 91 %) upon filtering the resulting precipitate after adding 15 ml water, washing with water and drying under vacuum. The polymer is marginally soluble in DMSO and NMP. DP=12, MW=3504. ^{1}H NMR (200 MHz, [D] DMSO): δ = 12.09 (d, 2 H), 8.54 (br, s, 2 H), 8.24 (br, s, 5 H), 7.57 (br, s, 1 H). Anal. calc. for $C_{16}H_{12}N_4O_2$ x 3.55 DMSO x 1.75 H_2O: C 46.15, H 6.17, N 9.32 S 18.93 found: C 45.94, H 5.95, N 9.28, S 18.87.



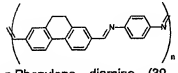
Terephthalic dicarboxylic acid hydrazide (98 mg, 0.51 mmol) was dissolved in 70 ml DMSO followed by 50 % aqueous solution of glutaric dialdehyde (110 mg, 0.55 mmol) and the reaction was allowed to stir at room temperature for a period of 18 hours. The polymer was isolated by filtering the precipitate formed after adding 14 ml water, washed with water then dried under vacuum to give a white solid (120 mg, 51 %). The polymer is marginally soluble in DMSO and NMP. ^{1}H NMR (200 MHz, [D] DMSO): δ = 11.55 (d, 2 H), 8.87 (br, s, 2 H), 7.79 (br, s, 4 H), 1.78 (br, s, 6 H). Anal. calc. for $C_{13}H_{14}N_4O_2$ x

1.05 DMSO: C 53.29, H 6.01, N 16.46, S 16.46 found: C 53.18, H 5.46, N 21.69, S 12.39.

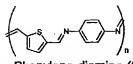
General method of polyimine synthesis

For activated monomers, typically 80 to 100 mg of the diamine monomer were charged into a 100 ml round bottom flask then dissolved in between 60 and 75 ml of the polymerization solvent to which is then added an exact stoichiometric amount of dialdehyde monomer. Suitable polymerization solvents are absolute ethanol, chloroform, methanol, anhydrous toluene, DMSO (methyl sulfoxide), DMF (N,N-dimethyl formamide), NMP (N-methyl pyrrolidinone), water, but not may also included others. For the polymers examined, DMSO promoted the fastest polymerization rates. A catalyst is not required for some monomers, but in general, the apparent rates of reaction are greatly accelerated with its use, typically trifluoroacetic acid or acetic acid. The reaction mixture is then heated between 90° – 110° C for a period between 12 to 24 hours. In the case of low boiling point solvents, the polymer is isolated by removing the solvent under reduced pressure and then dried under vacuum. For less volatile solvents, the polymers are subsequently used without isolation. For the polymerization in water, the reaction was typically done at room temperature under moderately alkaline conditions. An emulsion catalyst such as benzyltriethyl ammonium chloride, may also be used for imine polymerization involving hydrophobic and hydrophilic monomers.

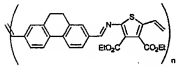
For less reactive monomers, the polymerization was undertaken as follows. Typically 150 mg of diamine monomer was dissolved in 10 ml of anhydrous toluene followed by three stoichiometric equivalents of 1,4-Diaza-bicyclo[2.2.2]octane (DABCO) under an argon atmosphere. To this was added 1.5 stoichiometric equivalents of titanium (IV) chloride then the reaction mixture refluxed after the addition of one stoichiometric equivalent of monomer dialdehyde for a period of 24 hours. The polymer precipitated from solution and was isolated by filtration then washed with toluene and chloroform.



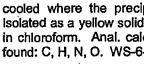
p-Phenylene diamine (39 g, 0.37 mmol) and 9,10-dihydro-phenanthrene-2,7-dicarbaldehyde (82 g, 0.37 mmol) were dissolved in 15 ml anhydrous toluene. The reaction mixture was refluxed under argon and protected from light for 18 hours. The solvent from the yellow mixture was removed under reduced pressure to yield the polymer as yellow powder then further dried under vacuum. The resulting polymer is insoluble in any common organic solvent. Anal. calc. for $C_{22}H_{16}N_2 \times 0.15\ H_2O$: C 84.94, H 5.28, N 9.01 found: C 83.97, H 4.32, N 9.90.



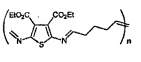
p-Phenylene diamine (98 g, 0.91 mmol) and thiophene-2,5-dicarbaldehyde (127 g, 0.91 mmol) were dissolved in 15 ml anhydrous toluene. The reaction mixture was refluxed under argon for 18 hours and protected from light. The solvent from the red mixture was removed under reduced pressure to yield the polymer as deep purple red flakes then further dried under vacuum. ^{1}H NMR (200 MHz, [D] DMSO): δ = 8.99 (s, 2 H), 8.87 (d, 2 H), 8.79 (d, 2H); 7.45 (br, s, 8 H), 7.18 (br, s, 12 H). Anal. calc. for $C_{12}H_8N_2S$ x 0.5 H_2O: C 65.84, H 4.10, N 12.66, S 14.49 found: C 65.80, H 3.52, N 11.89, S 13.58.



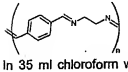
9,10-Dihydro-phenanthrene-2,7-dicarboxaldehyde (199 mg, 0.84 mmol) was dissolved 40 ml absolute ethanol to which was added thiophene-2,5-dicarbaldehyde (218 mg, 0.84 mmol). To this reaction mixture was added two drops of trifluoroacetic acid then the reaction mixture refluxed under argon for 24 hours. The yellow coloured mixture was cooled where the precipitate was isolated by vacuum filtration. The polymer was isolated as a yellow solid that was soluble in DMSO, DMF, NMP, and marginally soluble in chloroform. Anal. calc. for $C_8H_{14}O_7S_2$ (262.30): C 27.47, H 5.38, O 42.70, S 24.45 found: C, H, N, O. WS-6-38



In 7 ml anhydrous toluene was added 2,5-diamino-3,4-ethyl ester thiophene (146 g, 0.56 mmol) followed 1,4-diaza-bicyclo[2.2.2]octane (DABCO; 411 mg, 3.66 mmol) added under argon followed by titanium (IV) chloride (100 µl, 0.91 mmol). The temperature was raised then thiophene-2,5-dicarboxaldehyde (79 g, 0.56 mmol) dissolved in 10 ml anhydrous toluene was added and the mixture was refluxed under argon for 24 hours. The red wine coloured mixture was cooled and the precipitate was isolated by vacuum filtration. The polymer was isolated as deep blood red flakes readily soluble in alcoholic solvents, DMSO, DMF, and marginally soluble in chloroform. Anal. calc. for $C_{16}H_{14}N_2S_2$ x 35.85 H_2O: C 37.85, H 8.67, N 10.50, S 5.79 found: C 34.94, H 8.67, N 10.89, S 4.66.

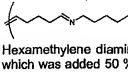


A 50 % aqueous solution of glutaric dialdehyde (464 mg, 2.31 mmol) was added to 2,5-diamino-3,4-diethyl ester thiophene (600 mg, 2.32 mmol) dissolved in 80 ml absolute ethanol. The solution was allowed to stir at room temperature for two days following the addition of a couple of drops of acetic acid. Eventually a red precipitate forms and is isolated by vacuum filtration then dried under vacuum. The title polymer is isolated as a red solid slightly soluble in DMSO and DMF. ^{1}H NMR (200 MHz, [D] DMSO): δ = 9.25 (br, s, 2 H), 7.80 (br, s, 4 H), 1.12 (br, s, 4 H), 1.06 (br, s, 2 H). Anal. calc. for $C_{15}H_{18}N_2O_4S$ x 1.35 H_2O: C 50.66, H 5.75, N 7.76, S 13.26 found: C 50.31, H 5.16, N 6.71, S 14.64.

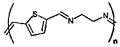


In 35 ml chloroform was added terephthalic dicarboxyaldehyde (284 mg, 2.12 mmol), ethylene diamine (150 µl, 2.24 mmol) and five drops of acetic acid and the resulting beige coloured heterogeneous solution was stirred at room temperature for 18 hours. The resulting precipitate was filtered, washed with water, and dried under vacuum to yield the polymer (202 mg, 73 %) as a yellow solid slightly soluble in DMSO and DMF. ^{1}H NMR (200 MHz, [D] DMSO): δ = 8.40 (br, s, 2 H), 8.32 (br, s, 2 H), 7.83 (br, s, 2 H), 1.81 (br, s, 4 H). Anal. calc. for $C10_8H_{10}N_2$ x 0.5 H_2O: C 74.35, H 7.89, N 13.09 found: C 75.92, H 6.37, N 14.49.

Terephthalic dicarboxaldehyde (446 mg, 3.32 mmol) and ethylene diamine (230 µl; 3.44 mmol) were dissolved in 100 ml absolute ethanol followed by two drops of trifluoroacetic acid. The solution was then refluxed for 18 hours then the solvent removed under reduced pressure to give the polymer as a yellow solid that was moderately soluble in DMSO and DMF. Anal. calc. for $C_{10}H_{10}N_2$ x 5.6 H_2O: C 56.08, H 6.71, N 6.36 found: C 56.08, H 6.02, N 6.94.

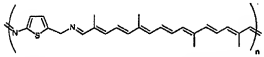


Hexamethylene diamine (578 mg, 4.97 mmol) was dissolved in 65 ml distilled water to which was added 50 % aqueous solution of glutaric dialdehyde (1.02 g, 5.09 mmol) then the white opaque heterogeneous solution was heated to 50^0 C for 12 hours. The precipitate formed was removed by vacuum filtration and washed with copious amounts of water then dried under vacuum. The polymer was isolated as a slightly yellow coloured solid (645 mg, 46 %) that is moderately soluble in DMSO and DMF. Anal. calc. for $C_{11}H_{20}N_2$ x 0.55 H_2O: C 70.17, H 10.45, N 11.90 found: C 69.83, H 11.18, N 15.54. ^{1}H NMR (200 MHz, [D] $CDCl_3$): δ = 8.04 (s, 1 H), 7.58 (m, 1 H), 6.1 (s, 1 H), 3.46 (t, 4 H), 2.62 (t, 8 H), 1.96 (t, 4 H), 1.9 (m, 4 H).

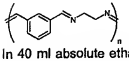


In 35 ml chloroform was added 2,5-thiophene dicarboxaldehyde (270 mg, 1.93 mmol), ethylene diamine (130 µl, 1.94 mmol) and five drops of acetic acid and the resulting orange coloured heterogeneous solution was stirred at room temperature for 18 hours. The resulting precipitate was filtered, washed with water, and dried under vacuum to yield the polymer (202 mg, 64 %) as a yellow solid slightly soluble in DMSO and DMF. ^{1}H NMR (200 MHz, [D] DMSO): δ = 9.90 (s), 8.47 (br, s, 2 H), 7.34 (br, s, 2 H), 3.56 (br, s, 2 H), 1.17 (br, s, 4 H). Anal. calc. for $C_8H_8N_2S$ x 0.55 H_2O: C 55.18, H 5.27, N 16.09, S 18.41 found: C 55.32, H 5.21, N S 15.73.

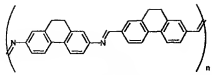
In 40 ml absolute ethanol was added 2,4-dithiophene carboxaldehyde (312 mg, 2.22 mmol), ethylene diamine (150µl, 2.22 mmol) and a drop of trifluoroacetic acid and the resulting orange coloured solution was refluxed for 18 hours. The solvent was removed to give the polymer as a yellowish oil that eventually solidifies and is slightly soluble in DMSO and DMF. DP = 13 , MW = 2132. ^{1}H NMR (200 MHz, [D] DMSO): δ = 9.90 (s), 8.47 (br, s, 2 H), 7.34 (br, s, 2 H), 3.56 (br, s, 2 H), 1.17 (br, s, 4 H). Anal. calc. for $C_8H_8N_2S$ x 4.3 H_2O: C 39.76, H 6.32, N 11.59, S 13.26 found: C 43.09, H 4.31, N 11.59, S 10.30.



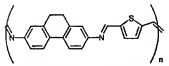
In absolute ethanol (50 ml) was dissolved 2,5-diamino-3,4-diethyl ester thiophene (99 mg, 0.38 mol) and crocetin dialdehyde (112 mg, 0.37 mmol) followed by a couple of drops of acetic acid. The blood red coloured solution was stirred at room temperature for 3 days where the solvent was then removed under reduced pressure. The red solid was further dried under vacuum to yield the polymer that is remotely soluble in DMSO, DMF, and chloroform. DP = 3, MW = 1632. ^{1}H NMR (200 MHz, [D] $CDCl_3$): δ = 7.60 (s, 2 H), 6.89 (br, s, 10 H), 4.43 (br, s, 4 H), 1.47 (br, s, 18 H). Anal. calc. for $C_{26}H_{34}N_4O_2$ x 5.55 H_2O: C 58.42, H 8.50, N 10.48 found: C 54.99, H 6.01, N 9.53.



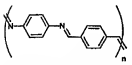
In 40 ml absolute ethanol was added isoterephthalic dicarboxyaldehyde (285 mg, 2.12 mmol), ethylene diamine (145 µl, 2.12 mmol) and five drops of trifluoroacetic acid and the resulting yellow coloured solution was stirred at reflux for 18 hours. The resulting precipitate was filtered, washed with water, and dried under vacuum to yield the polymer as a yellow solid slightly soluble in DMSO and DMF. ^{1}H NMR (200 MHz, [D] DMSO): δ = 8.40 (br, s, 2), 8.32 (br, s, 2), 7.83 (br, s, 2 H), 1.81 (br, s, 4 H). Anal. calc. for $C_{10}H_{10}N_2$ x 0.55 H_2O: C 73.96, H 7.90, N 13.02 found: C 72.39, H 6.27, N 14.22.



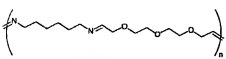
9,10-Dihydro-phenanthrene-2,7-dicarbaldehyde (81 mg, 0.34 mmol) and 9,10-dihydro-phenanthrene-2,7-diamine (72 mg, 0.34 mmol) were dissolved in 50 ml anhydrous toluene. The reaction mixture was refluxed under argon for 18 hours and protected from light. The solvent from the yellow mixture was removed under reduced pressure to yield the polymer as a bright yellow powder red flakes then further dried under vacuum and is insoluble in any organic solvent. Anal. calc. for $C_{30}H_{22}N_2 \times 0.35\ H_2O$: C 86.45, H 5.59, N 6.72 found: C 85.46, H 4.35, N 6.26.



2,5-Thiophene dicarboxaldehyde (70 mg, 0.50 mmol) and 9,10-dihydro-phenanthrene-2,7-diamine (104 mg, 0.49 mmol) were dissolved in 40 ml anhydrous toluene. The reaction mixture was refluxed under argon and protected from light for 18 hours. The solvent from the yellow mixture was removed under reduced pressure to yield the polymer as a yellow solid further dried under vacuum and is insoluble in any organic solvent. Anal. calc. for $C_{20}H_{14}N_2S \times 0.1\ H_2O$: C 75.97, H 4.53, N 8.86, S 10.14 found: C 75.91, H 3.14, N 7.95, S 8.73.

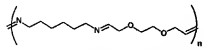


p-Phenylene diamine (928 mg, 8.59 mmol) was dissolved in 100 absolute ethanol followed by terephthalic dicarboxaldehyde (1.15 g, 8.59 mmol). The reaction was refluxed under argon for 30 hours under argon and protected from light. The solvent was removed under reduced pressure and dried to give the polymer as a yellow solid which is not readily soluble in any organic solvent. Cald. $C_{14}H_{10}N_2 \times 0.45\ H_2O$: C 80.48, H 4.97, N 13.41 found 79.83, H 4.50, N 13.59.

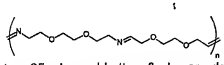


To an aqueous solution of freshly prepared 2-[2-[2-(2-hydroxy-ethoxy)-ethoxy]-ethoxy]-ethanol was added 1,6-diaminohexane (1.16 g, 9.98 mmol) at room temperature. Within

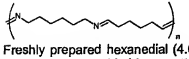
30 minutes, the solution becomes troubled and after 4 hours, the polymer begins to precipitate. After an additional 3 hours of stirring, the precipitate was filtered by vacuum filtration and washed with an abundant amount of water then dried under vacuum to give 1.64 g (54 %) of the polymer as a white solid. ^{1}H NMR (200 MHz, [D] DMSO): δ = 8.29 (s, 2 H), 3.42-3.52 (m, 10 H), 2.49-2.63 (m, 8 H), 1.30-1.48 (m, 6 H). Cald. $C_{14}H_{26}O_3N_2$ x 2.3 $H_2$0: C 55.23, H 8.95, N 7.62 found 53.93, H 9.89, N 8.98.



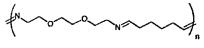
To freshly prepared [2-(2-oxo-ethoxy)-ethoxy]-acetaldehyde (3.70 mmol) in approximately 125 ml aqueous sodium hydrogen carbonate was added hexamethylene diamine (420 mg, 3.70 mmol). The reaction mixture was allowed to stir at room temperature for 36 hours eventually giving a yellow colour. The reaction medium was poured onto 500 ml absolute ethanol and sodium hydrogen carbonate filtered off. The solvent from the yellow filtrate was removed under reduced pressure to give the title polymer as a yellow. ^{1}H NMR (200 MHz, [D] DMSO): δ = 8.46 (s, 2 H), 3.49 (br, s, 8 H), 1.26 (br, s, 12 H).



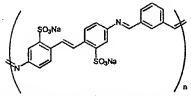
In a 25 ml round bottom flask was added 2-[2-(2-amino-ethoxy)-ethoxy]-ethylamine (0.2 ml, 1.37 mmol) followed by 0.26 mM aqueous solution of [2-(2-oxo-ethoxy)-ethoxy]-acetaldehyde (5 ml, 1.43 mmol) followed by 2 ml of 2 M aqueous sodium hydroxide then diluted with 15 ml water. The reaction mixture turned fluorescent yellow within minutes and was allowed to stir at room temperature for 36 hours before the solvent was removed under reduced pressure leading to a yellow solid. ^{1}H NMR (200 MHz, [D] D_2O): δ = 8.47 (m, 2 H), 8.11 (m, 2 H), 3.35 (m, 4 H), 3.05 (m, 8 H), 2.67 (m, 4 H), 2.26 (m, 4 H).



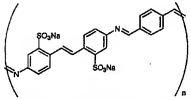
Freshly prepared hexanedial (4.69 mmol) was diluted in 100 ml of absolute ethanol to which was then added hexamethylene diamine (532 mg, 4.57 mmol). The solution was then refluxed for 24 hours after which the solvent was removed under pressure to afford the polymer as a lightly Indian red coloured solid. . ^{1}H NMR (200 MHz, [D] $CDCl_3$): δ = 8.04 (s, 2 H), 7.58 (br, s, 2 H), 3.32 (m, 4 H), 2.56 (m, 6 H), 1.24 (m, 8 H).



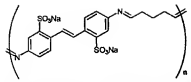
To freshly prepared 1,6-hexanal (4.49 mmol) by oxidation of 1,2-cyclohexane-diol was added 2-[2-(2-amino-ethoxy)-ethoxy]-ethylamine (700 µl, 4.79 mmol) in 50 ml absolution methanol and the mixture refluxed for 24 hours. The solvent was removed under reduced pressure and the resulting brown oil dried under high vacuum. ^{1}H NMR (200 MHz, [D] DMSO): δ = 8.11 (s, 1 H), 7.08 (s, 1H), 3.43 (m, 12 H), 1.55 (m, 8 H).



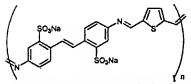
4,4'-Diaminostilbene-2,2'-disulfonic acid (152 mg, 0.41 mmol) was added to a round bottom flask along with 30 ml water to give a suspension. A few of drops of 2M sodium hydroxide were added to render the reaction medium alkaline and transform the diamino reagent into the sulfonic salt that is soluble in the aqueous solvent. Approximately 15 ml of THF was then added followed by the addition of the isoterephthalic dicarboxaldehyde (56 mg, 0.42 mmol) dissolved in 3 ml THF. The colour immediately becomes yellow and the reaction was allowed to stir at room temperature for 30 minutes before a catalytic amount of benzyltriethyl ammonium chloride was added. The reaction mixture was stirred at room temperature for two days then the solvent removed under reduced pressure to give the polymer as a yellow solid. λ_{max} (water): 227 and 338 nm. ^{1}H NMR (200 MHz, [D] DMSO): δ = 8.80 (br, s, 2 H), 8.15 (br, s, 4 H), 7.80 (br, s, 4 H), 7.39 (br, s, 4 H).



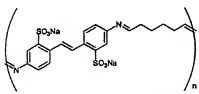
4,4'-Diaminostilbene-2,2'-disulfonic acid (160 mg, 0.45 mmol) was added to a round bottom flask along with 30 ml water to give a suspension. A few of drops of 2M sodium hydroxide were added to render the reaction medium alkaline. Approximately 15 ml of THF was then added followed by the addition of the terephthalic dicarboxaldehyde (61 mg, 0.45 mmol) dissolved in 3 ml THF. The colour immediately becomes red and the reaction was allowed to stir at room temperature for 30 minutes before a catalytic amount of benzyltriethyl ammonium chloride was added. The reaction mixture was stirred at room temperature for two days then the solvent removed under reduced pressure to give the polymer as a red solid. λ_{max} (water): 262 and 339 nm. DP = 20, MW = 10 000. ^{1}H NMR (200 MHz, [D] DMSO): δ = 8.80 (br, s, 2 H), 8.15 (br, s, 4 H), 7.80 (br, s, 4 H), 7.39 (br, s, 4 H). Anal. cald. $C_{22}H_{14}O_6N_2S_2Na_2$ x 11 H_2O: C 37.18, H 5.11, N 3.94, S 9.02 found C 36.93, H 4.81, N 3.95, S 8.93.



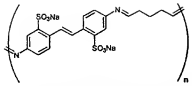
A total of 60 ml distilled water along with a few drop of 2M sodium hydroxide was used to dissolved 4,4'-diaminostilbene-2,2'-disulfonic acid (216 mg, 0.58 mmol) to which was added 50 % aqueous glutaric dialdehyde (117 mg, 0.58 mmol). The solution was stirred at room temperature fro two days then the solvent removed to give the polymer as a yellow coloured solid. λ_{max} (water): 225 and 340 nm. DP = 22, MW = 10 498. ^{1}H NMR (200 MHz, [D] D_2O): δ = 7.80 (br, s, 6 H), 7.35 (br, s, 2 H), 7.04 (br, s, 2 H), 1.75 (br, s, 6H).



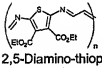
A volume of 60 ml distilled water and a few drops of 2M sodium hydroxide was required to dissolved 4,4'-diaminostilbene-2,2'-disulfonic acid (155 mg, 0.41 mmol). After the addition of 40 ml THF, was added 2,5-thiophene dicarboxaldehyde (58 mg, 0.42 mmol) along with a catalytic amount of benzyltriethyl ammonium chloride. The red coloured solution was stirred at room temperature for two days then the solvent removed under reduced pressure to afford the polymer as a red solid. λ_{max} (water): 305 and 338 nm. ^{1}H NMR (200 MHz, [D] DMSO): δ = 8.92 (br, s, 2 H), 8.21 (br, s, 2 H), 7.80 (br, s, 6 H), 7.39 (br, s, 2 H). Anal. cald. $C_{20}H_{12}O_6N_2S_3Na_2$ x 7.2 H_2O: C 37.06, H 4.11, N 4.32, S 14.84 found C 37.27, H 3.90, N 4.28, S 14.62.



In roughly 10 ml of water was added 4,4'-diaminostilbene-2,2'-disulfonic acid (1.85 g, 4.99 mmol) and then solubilized with the addition of solid sodium hydroxide. To this lightly yellow coloured solution was added freshly freshly prepared 1,6-hexanedial (6.12 mmol) via oxidation of 1,6-cyclohexandiol and the reaction stirred at room temperature for 18 hours. The solvent was removed under reduced pressure to afford the title polymer as a brown oil. ^{1}H NMR (200 MHz, [D] DMSO): δ = 7.70 (s, 2), 7.33 (d, 2 H), 7.10 (d, 2 H), 6.54 (d, 2 H), 5.09 (s, 2 H), 3.49 (t, 4 H), 1.22 (d, 4 H).



In approximately 25 ml water was added 4,4'-diaminostilbene-2,2'-disulfonic acid (1.79 g, 4.83 mmol) and then solubilized by the addition of solid sodium hydrogen carbonate. To this lightly yellow coloured solution was added glutaric dialdehyde (1.02 g, 5.09 mmol) where the colour immediately became light green. The reaction was allowed to stir for 18 hours at room temperature than poured onto 300 ml absolute methanol. The polymer was filtered and recovered as a moss green latex gel that became solid upon removal of the residual solvent by reduced pressure. The title polymer is only soluble in water and mildly soluble in DMSO. λ_{max} (water): 346 nm. ^{1}H NMR (200 MHz, [D] D_2O): δ = 7.80 (m, 8 H), 7.40 (m, 2 H), 7.06 (m, 2 H), 3.09 (m, 4 H), 1.48 (m, 2 H).



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2,5-Diamino-thiophene-3,4-dicarboxylic acid diethyl ester (48.3 mg, 0.19 mmol) was dissolved in 30 ml absolute ethanol. To the resulting yellow coloured solution was added 40 % aqueous glycoxaldehyde solution (110 mg, 0.75 mmol) and then the solution was refluxed for 24 hours. The solvent was removed under vacuum to afford the polymer as a bright red solid. λ_{max} (DMSO): 305, 418 and 497 nm.

Method of polyhydrazone monomer exchange

Typically a polymeric stock solution comprising 24 mg of polyhydrazone was prepared by dissolving it in 2.5 ml deuterated DMSO through a process of heating then ultrasonication. Separately, 7 mM stock solutions of dialdehyde monomer and dihydrazide monomers were prepared in deuterated DMSO. Exactly 0.3 ml of the polymer solution was charged into a NMR tube followed by 0.05 ml of either the dialdehyde or dihydrazide stock solution. The resulting mixture is then lightly heated between 50° and 75°C for a period of between 0.5 minutes and a maximum of 2 minutes to induce the monomer exchange within the polymer and observed by NMR. A catalytic amount, being less than 1 µl, of trifluoroacetic acid along with mild heating is required to exchange the polymeric monomer units of thermodynamically stable polyhydrazones.

In an NMR tube was dissolved the polyhydrazone derived from adipic acid dihydrazide and glutaric dialdehyde (7.1 mg) in 0.5 ml of deuterated DMSO with heating and sonication. To this was added isoterephthalic dicarboxaldehyde (0.95 mg, 8 x 10^{-3}

mmol) and the NMR spectrum recorded. The polymeric solution was heated mildly for 30 seconds and the NMR spectra recorded, after different heating intervals, at room temperature that clearly showed new hydrazone protons in the chemical shift region of 12.13 and 8.56 ppm resulting from dialdehyde monomer exchange forming a new polyhydrazone.

A volume of 0.5 ml of a stock solution of the polyhydrazone derived from adipic acid dihydrazide and glutaric dialdehyde (49 mg in 2.5 ml) was added to a NMR tube. To this was added 0.05 ml of a stock solution of isoterephthalic dicarboxaldehyde (7 mmol) and NMR spectrum recorded. The polymeric solution was mildly heated for 30 seconds and the NMR spectra recorded clearly showed new hydrazone protons in the chemical shift region of 11.59 and 8.32 ppm resulting from dihydrazide monomer exchange of the new polyhydrazone.

The polyhydrazone derived from isoterephthalic carboxylic acid dihydrazide and glutaric dialdehyde (0.5 ml of stock solution of 24.1 mg in 2.5 ml) in deuterated DMSO was placed in a NMR tube. To this was added 0.05 ml of a stock solution of isoterephthalic dicarboxaldehyde (7 mmol) and the NMR spectrum recorded. The polymeric solution was heated mildly for 30 seconds after the addition of 1µl of deuterated trifluoroacetic acid and the NMR spectra recorded at different intervals at room temperature which clearly showed new hydrazone protons in the chemical shift region of 12.13 and 8.56 ppm resulting from dihydrazide monomer exchange leading to a new polyhydrazone.

A total of 0.5 ml of the polyhydrazone derived from isoterephthalic carboxylic acid dihydrazide and isoterephthalic dicarboxaldehyde (24.1 mg in 2.5 ml) in deuterated DMSO was placed in a NMR tube. A volume of 0.05 ml of a stock solution of adipic acid dihydrazide (7 mmol) was added and the NMR spectrum recorded. The polymeric solution was heated mildly for 30 seconds after the addition of 1µl of deuterated trifluoroacetic acid and the NMR spectra recorded at different intervals at room temperature. The spectrum clearly showed new hydrazone protons in the chemical shift region of 11.43 and 7.99 ppm resulting from dihydrazide monomer exchange leading to a new polyhydrazone.

A stock solution in DMSO of the polyhydrazone derived from isoterephthalic carboxylic acid dihydrazide and glutaric dialdehyde (3.5 mg in 5 ml, ca. 0.33 mM) and a stock solution of crocetin dialdehyde (4.3 mM) were used. In a UV-Visible spectrophotometric cuvette was added 1.5 ml (0.5 mmol) of the polymeric solution, 1.5 ml (0.65 mmol) of the dialdehyde solution and 2 µl of acetic acid. The cuvette was heated to 75° C and the new polymer formed resulting from dialdehyde monomer exchange was observed at 345 and 335 nm. A first order rate constant of 3.2×10^{-3} s^{-1} was measured for the rate of monomer exchange.

Method of polyimine monomer exchange

The exchange reaction involving monomers with the polymer cannot be easily followed by NMR as is the case with polyhydrazones. The imine NMR chemical shifts of the

exchanged and unexchanged polymer cannot be easily resolved. UV-visible spectroscopy was alternatively used to monitor the monomer exchange within polyimines where a coloured polymer was either formed or decomposed through monomer exchange.

The polyimine derived from 2,5-thiophene dicarboxaldehyde and ethylene diamine (0.98 mg, 0.001 mM) and 2,5-diamino-thiophene-3,4-dicarboxylic acid diethyl ester (2.2 mg, 0.01 mmol) were dissolved in 3 ml of DMSO in a UV-visible cuvette followed by 2 µl acetic acid. The cuvette was thermostated at 75° C and the change in absorbance monitored at 440 nm and 470 nm leading to a rate constant of exchange of 3×10^{-2} M s^{-1}.

The polyimine derived from 2,5-diamino-thiophene-3,4-dicarboxylic acid diethyl ester and thiophene-2,5-dicarboxaldehyde was dissolved in 3 ml DMSO followed by the addition 2,3-bis-dodecyloxy-succinic acid dihydrazide (0.5 mg, 9.9×10^{-4} mmol) and 2 µl acetic acid. The solution was heated at 75° and 100° C and the decrease in the absorbance at 482 nm corresponding to the initial polyimine was observed denoting the occurrence of diamine monomer exchange.

In a UV-visible cuvette was charged in 1.6 ml of a stock solution (0.18 mM) of 9,10-dihydro-phenanthrene-2,7-dicarbaldehyde, 1.6 ml of a stock solution (0.21 mM) of 2,5-diamino-thiophene-3,4-dicarboxylic acid diethyl ester and 1 µl of trifluoroacetic acid. The reaction mixture was polymerized at 50° C for 48 hours. Upon polymerization completion, either 2 or 5 stoichiometric equivalents of isoterephthalic dicarboxaldehyde were added to the cuvette along with 1 µl of trifluoroacetic acid. The decrease in the absorbance monitored at 442 nm over time indicated the dialdehyde monomer exchange within the polyimine. Rate constants of exchange of 4.4×10^{-6} s^{-1} and 5.1×10^{-6} s^{-1} were observed for 2 or 5 stoichiometric equivalents of dialdehyde added, respectively.

To the polyimine derived from 9,9-dihexyl-9H-fluorene-2,7-dicarbaldehyde and cyclohexane-1,4-diamine in NMP (0.52 mM) was further added 2,5-diamino-thiophene-3,4-dicarboxylic acid diethyl ester in 0.5, 1, 5, and 10 stoichiometric equivalents along with 1 µl of trifluoroacetic acid. The reaction mixture was placed in UV-visible cuvettes, heated at 75° C and the change in absorbance at 422 nm monitored indicating diamine monomer exchange. The rate of exchange was found to be first order regarding the diamine to be incorporated into the polyimine of 5.5×10^{-5} s^{-1} and $9.5 \times 10^{-5} s^{-1}$ for 5 to 10 equivalents, respectively.

Approximately 10 mg of the polymer derived from 4,4'-diaminostilbene-2,2'-disulfonic acid and glutaric dialdehyde was dissolved in 10 ml water with the aid of sonication and mild heating. To the resulting green coloured solution (λ_{max} = 346 nm) was added an equivalent amount of DMSO followed by a stoichiometric amount of 2,5-thiophene dicarboxaldehyde. Within a few minutes of adding the aldehyde the green colour is replaced by a pink one (λ_{max} = 532 nm) corresponding to the new polymer incorporating the thiophene unit. A change in fluorescence is equally observed with incorporation of

the thiophene unit from $\lambda_{emission}$ = 435 nm to $\lambda_{emission}$ = 450 nm at $\lambda_{excitation}$ = 350 nm. Alternatively, the thiophene unit can be dissolved into a minimum amount of DMSO or other water miscible solvents, then added directly to the aqueous polymer solution followed by mild shaking to ensure monomer exchange. The rate of exchange is faster when DMSO is added to the aqueous environment as a co-solvent.

The polymer derived from thiophene dicarboxaldehyde and ethylene diamine was solubilized in dichloromethane upon sonicating yielding a yellow heterogeneous solution. An equal volume of water containing 4,4'-diaminostilbene-2,2'-disulfonic acid solubilized through the addition of sodium carbonate was added to the dichloromethane solution. To the resulting biphasic solution was added a trace amount of trifluoroacetic acid. Gradually the thiophene dicarboxaldehyde migrates to the aqueous layer resulting in a new water soluble polyimine confirmed by the formation of a pink (λ_{max} = 537 nm) colour in the aqueous layer compounded with a new fluorescence at $\lambda_{emission}$ = 420 nm at $\lambda_{excitation}$ = 350 nm. The yellow colour associated with the polymer from the organic phase fades while this layer also becomes transparent.

General method of polyimine polymer exchange

The general method of polymer exchange maybe exemplified as follows. To the polyimine derived from 2,5-diamino-thiophene-3,4-dicarboxylic acid diethyl ester and isoterephthalic dicarboxaldehyde, prepared in DMSO and not isolated, was added the solid polyimine derived from thiophene-2,5-dicarboxaldehyde and ethylene diamine, which was insoluble. A trace amount of trifluoroacetic acid was added and the reaction mixture was heated between 50° and 90° C for a brief period of time. Eventually the insoluble polyimine becomes soluble by monomer exchange and the slight green colour is replaced by a deep red colour due to the formation of a conjugated polymer by polymer cross-monomer exchange.

Claims

What is claimed is:

1. Polymers capable of sustaining and/or promoting a process involving the exchange of the regular repeating monomer units presented in the form of a polyhydrazone or a polyimine, polymerized by repeating alternating units of dihydrazides and/or diamines and dialdehydes, but not limited to these two polymers and may also include other alternating co-polymers, defined as *Dynamers*.
2. The process of exchanging the regular repeating monomer units of a polyhydrazone or polyimine, polymerized by the condensation of alternating units of dihydrazides and/or diamines and dialdehydes, but not limited to these two polymers and may also include other alternating co-polymers, defined as *Dynamerization*.
3. The process of incorporating a dialdehyde monomer unit into the polymeric backbone of a polyhydrazone which itself is the result of polycondensation of repeating alternating units of dihydrazides and dialdehydes.
4. The process of exchanging the regular repeating dihydrazide monomer units of a polyhydrazone polymerized by repeating alternating units of dihydrazides and dialdehydes.
5. The process of exchanging the regular repeating dialdehyde monomer units of a polyimine polymerized by repeating alternating units of diamines and dialdehydes.
6. The process of exchanging the regular repeating diamine monomer unit of a polyimine polymerized by repeating alternating units of diamines and dialdehydes.
7. The process of exchanging the regular repeating diamine monomer unit of a polyimine polymerized by repeating alternating units of diamines and dialdehydes by a dihydrazide.
8. The process of exchanging the regular repeating monomer unit of a polyimine polymerized by repeating alternating units of diamines and dialdehydes.
9. The process of exchanging the regular repeating monomer units of a polyimine whereby the polymer's solubility has changed from hydrophobic to hydrophilic or *vice versa*.
10. The process of exchanging the regular repeating monomer units of a polyimine or polyhydrazone whereby the polymer's colour has changed.
11. The process of exchanging the regular repeating monomer units of a polyimine or whereby the polymer's degree of conjugation has changed.
12. The process of exchanging the regular repeating monomer units of a polyimine or polyhydrazone whereby the polymer's fluorescence has changed.

13. The process of exchanging the regular repeating monomer units of a polyimine or polyhydrazone whereby the polymer's physical properties have changed.

14. The process by which exchanging the regular repeating monomer units of a Dynamer changes its solubility for a given solvent.

15. The process of re-introducing the original regular repeating monomer units of a polyimine or polyhydrazone that were previously exchanged by the dynamerization process whereby regenerated the original polymer.

16. The process of exchanging the fundamental repeating units, known as cross-Dynamerization, of a polyimine in the presence of another polyimine by the use of acid catalysis and heat leading to two new polyimines.

17. The process of exchanging the fundamental repeating units, known as cross-Dynamerization, of a polyhydrazone in the presence of another polyhydrazone by the use of acid catalysis and heat leading to two new polyhydrazones.

18. The process of exchanging the fundamental repeating units, known as cross-Dynamerization, of a polyimine in the presence of polyhydrazone by the use of acid catalysis and heat leading to a new polyhydrazone and polyimine, respectively.

19. The process by which the processes of claims 1-18 make use of other reversible covalent bond forming reactions (such as disulfide, aldol, boronic ester formation, olefin metathesis, etc.) in addition to carbon-nitrogen double bond formation, are implemented to generate dynamic polymers.